



US007858667B2

(12) **United States Patent**
Hu et al.(10) **Patent No.:** US 7,858,667 B2
(45) **Date of Patent:** Dec. 28, 2010(54) **ALCOHOL SYNTHESIS FROM CO OR CO₂**(75) Inventors: **Jianli Hu**, Kennewick, WA (US); **Robert A. Dagle**, Richland, WA (US); **Jamelyn D. Holladay**, Kennewick, WA (US); **Chunshe Cao**, Houston, TX (US); **Yong Wang**, Richland, WA (US); **James F. White**, Richland, WA (US); **Douglas C. Elliott**, Richland, WA (US); **Don J. Stevens**, Richland, WA (US)(73) Assignee: **Battelle Memorial Institute**, Richland, WA (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 1046 days.

(21) Appl. No.: **11/611,160**(22) Filed: **Dec. 15, 2006**(65) **Prior Publication Data**

US 2007/0161717 A1 Jul. 12, 2007

Related U.S. Application Data

(60) Provisional application No. 60/751,144, filed on Dec. 16, 2005, provisional application No. 60/823,093, filed on Aug. 21, 2006.

(51) **Int. Cl.****C07C 27/00** (2006.01)(52) **U.S. Cl.** **518/715; 518/706; 518/716**(58) **Field of Classification Search** **518/706, 518/715, 716**

See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

- 4,119,656 A * 10/1978 Poutsma et al. 518/715
4,122,110 A 10/1978 Sugier et al.
4,831,060 A 5/1989 Stevens et al.
2003/0185721 A1 10/2003 Wang et al.
2004/0223908 A1 11/2004 Holladay et al. 423/648.1

FOREIGN PATENT DOCUMENTS

- EP 0034767 2/1981
EP 0152314 A2 8/1985
EP 0483919 A2 5/1992

GB 1296212 11/1972

OTHER PUBLICATIONS

Sahibzada et al., methanol synthesis from carbon dioxide/hydrogen over Pd-promoted CuO/ZnO/Al2O₃, (Chemical Abstract 123: 148523 (1995).*

Partial International Search Report for PCT/US2006/047935, mailed May 31, 2007.

Chin et al., "Preparation of a novel structured catalysts bed on aligned carbon nanotube arrays for a microchannel Fischer-Tropsch synthesis reactor," Catal. Today 110 (2005) 47-52.

Extended European Search Report, EP 08009880.9, mailed Oct. 10, 2008.

European Written Opinion, EP 08009880.9, mailed Oct. 10, 2008.

International Search Report for PCT /US2006/047935, mailed Aug. 21, 2007.

Hu et al., (2005) "Conversion of Biomass Syngas to DME Using a Microchannel Reactor" Ind. Eng. Chem. Res. pp. 1722-1727.

Yin et al., (2005) "Characteristics of the Synthesis of Methanol Using Biomass-Derived Syngas" Energy & Fuels 19, pp. 305-310.

Inui et al., (1998) "Effective Synthesis of Ethanol from CO₂ on Polyfunctional Composite Catalysts" Catalysis Today 45, pp. 209-214.

Ishiguro et al.,(1998) "Syngas Conversion using Rh VO₄ and Rh₂MnO₄ Catalysts: Regeneration and Redispersion of Rh Metal by Calcination and Reduction Treatments" Catalysis Today 45, pp. 197-201.

Jong et al., (1990) "Highly Dispersed Rh/ SiO₂ and Rh/ MnO/SiO₂ Catalysts" Journal of Catalysis 124, pp. 520-529.

Elliott et al., (1988) "Mechanism of Ethanol Formation from Syntheses Gas Over CuO/ZnO/Al₂O₃" Journal of Catalysts 114, pp. 90-99.

Imoto et al., "The Reduction of Zinc Oxide by Hydrogen III. The Effect of Nitrogen on the Reduction," J. Chem. Soc. Japan, pp. 441-444 (1964).

Sahibzada et al., "Hydrogenation of carbon dioxide to methanol over palladium-promoted Cu/ZnO/Al₂O₃ catalysts," Catal. Today 29 (1996) 367-372.

* cited by examiner

Primary Examiner—Jafar Parsa

(74) *Attorney, Agent, or Firm—Frank Rosenberg; Derek H. Maughan*

(57) **ABSTRACT**

Methods for producing alcohols from CO or CO₂ and H₂ utilizing a palladium-zinc on alumina catalyst are described. Methods of synthesizing alcohols over various catalysts in microchannels are also described. Ethanol, higher alcohols, and other C₂₊ oxygenates can produced utilizing Rh—Mn or a Fisher-Tropsch catalyst.

32 Claims, 5 Drawing Sheets